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Irradiation impact on the leaching behavior of HLW glasses

Magaly Tribet[a]*, Séverine Rolland[a], Sylvain Peuget[a], Véronique Broudic[a], Magali Magnin[a], Thierry Wiss[b], Christophe Jégou[a]

[a]*CEA/DEN/DTCD/SECM/LMPA, BP 17171, 30207 Bagnols sur Cèze cedex, France*
[b]*European Commission, Joint Research Centre, Institute for Transuranium Elements, Karlsruhe, Germany*

Abstract

Fission products and minor actinides arising from spent fuel reprocessing are immobilized in a borosilicate matrix known as high level nuclear waste glass (i.e. HLW glass). Glass packages are intended eventually for disposal in a geological repository. The long-term behavior of HLW glass subjected to radiation by long-life radionuclides must thus be investigated with respect to geological disposal. The present article focuses on HLW glass alteration under irradiation conditions by providing a general description of the methodology and illustrating it through examples. The scientific approach adopted to study irradiation potential effects combines experiments performed on radionuclide-doped borosilicate glasses and non radioactive glasses externally irradiated, focusing on all the different leaching stages (initial, drop and residual steps). Different parameters, such as the cumulative dose, the dose rate, the electronic and the ballistic impacts, are taken into account. As under disposal conditions the glass radioactivity will be quickly governed by alpha decay (after 300 years), the results presented here to illustrate the methodology concern the behavior of alpha-doped glasses. Concerning the initial alteration rate, both the alpha activity and the alpha cumulative dose have been studied and no significant effects have been observed. The structural variations observed on the irradiated solid are thus not important enough to induce any changes in the initial chemical reactivity between glass and water. Concerning the drop and residual alteration steps, the behavior of a ^{239}Pu-doped glass having an alpha dose rate corresponding to a HLW glass after around 1500 years has shown no effect on the kinetics, nor on the altered layer morphology. Moreover, the plutonium appears to be highly retained in the alteration layer (~ 95%).

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Keywords: Nuclear glass; alpha-doped glass; radioactivity; leaching, dissolution rate

* Corresponding author. Tel.: +33-4-66-33-91-52.
E-mail address: magaly.tribet@cea.fr

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1. Introduction

Like some other countries, France has opted to reprocess spent fuel from its civilian nuclear power plants. Fission products and minor actinides arising from spent fuel reprocessing are immobilized in a borosilicate matrix known as HLW glass. Glass packages have been produced and are intended eventually for disposal in a geological repository. Under repository conditions, radionuclides release from the glass will begin only when water comes into contact with the matrix. Since leaching is the most probable process by which radionuclides can be released from the glass, it is particularly important to study the mechanisms and kinetics of glass alteration in contact with water.

The alteration of SON68 glass (nonradioactive surrogate of the French R7T7 glass) has been extensively studied during the last thirty years. Different kinetic stages have been observed during borosilicate glass alteration in a closed environment, and the corresponding key mechanisms have been proposed [Vienna et al. (2013)]:

- Ion exchange reactions involving the mobile glass constituents (alkalis, boron, etc.) and hydrogenated species (H_2O, H_3O^+) occur rapidly during the initial instants;
- Hydrolysis of the glass network resulting in the existence of an initial glass dissolution rate;
- Creation of an amorphous layer at the glass/solution interface caused by the difference between the two kinetics previously described, regardless of the alteration conditions. This layer is gradually reorganized by hydrolysis and condensation mechanisms. This amorphous layer constitutes a barrier against the transport of water toward the glass and of solvated glass ions into solution, inducing a rate drop regime. The existence of this transport-inhibiting effect rapidly causes this layer to control glass alteration. It is called 'passivating reactive interphase' (PRI) in accordance with its properties;
- The last step is the residual rate regime in which glass dissolution results from the formation of secondary aluminosilicate crystalline phases such as phyllosilicates and the interdiffusion of water and solvated ions through the PRI. This long-term alteration rate would be the dominant alteration phenomenon under geological disposal conditions in the long term [Poinssot et al. (2012)]
- Finally, a resumption of alteration can occur in case of strong secondary crystalline phases precipitation (zeolite). For the R7T7 glass, this phenomenon has rarely been observed, and only for pH > 10,5 and/or T > 90°C and are not self-supported

Moreover, it must be kept in mind that a HLW glass is subjected to irradiation-induced stresses whose consequences must be assessed to guarantee the material behavior over time, under disposal conditions. In general, irradiation can modify solid properties (by creating defects in its structure…) as well as solution equilibria (water radiolysis, changes in the thermodynamical equilibria, redox potential modification…). To fully understand the potential irradiation effects, two parameters must be taken into account:

- First, the potential influence of the irradiation damage (i.e. cumulative dose) on the chemical reactivity of glass and PRI. This damage of the solid accumulates during the glass life span, including the period before groundwater site saturation;
- Second, the influence of the irradiation dose rate on both the solids (pristine glass and PRI) through changes in diffusion and/or sorption properties and in the solution chemistry (radiolysis).

Nomenclature

PRI	Passivating reactive interface
r_0	Initial alteration rate
r_r	Residual alteration rate

2. Scientific approach

The scientific approach adopted to study irradiation potential effects combines experiments performed on radionuclide-doped borosilicate glasses and external irradiations of non radioactive samples, focusing on all the different leaching stages (initial, drop and residual steps).

2.1. Radionuclide-doped glasses

Several doped materials were elaborated to investigate both the effects of the integrated dose and of the dose rate on glass leaching behavior. Thus, different isotopes at varying concentrations have been used in order to cover a wide range of dose rates, as presented in figure 1, presenting the dose rate of the studied glasses compared to the dose rate evolution of a typical R7T7 glass versus time. The dose rate of some studied glasses is higher than those of current industrial glasses at the time of water arrival, in order to exacerbate the irradiation effect and to reveal a potential change in the kinetics. The influence of the radiation nature (α, β, γ) has also been taken into account through the nature of the dopant element (Tc or actinides). In addition, some leaching experiments have been performed long time after the glass elaboration in order to cumulate important doses and to evaluate the effect of this parameter.

The use of radionuclide-doped glasses also allows to understand the radionuclide behavior during the glass leaching and to assess the retention properties of the alteration products [Rolland et al. (2013)][Advocat et al. (2001)][Jollivet et al. (2005)]. Finally, doped glass leaching experiments can also be carried out under realistic disposal conditions [Valcke et al. (2006)].

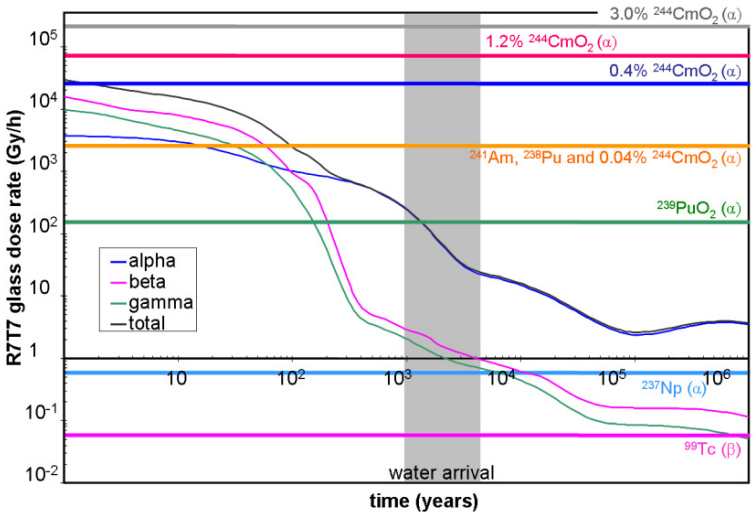

Fig. 1. alpha, beta, gamma and total dose rate evolution versus time for the typical R7T7 glass. Comparison with the different doped glasses studied.

2.2. External irradiation of the system

External irradiations are performed to complete studies on doped materials. Different kind of facilities, radiations and methodologies can be used. For example, an inactive sample can first be irradiated and then be leached (short irradiation time), or the leaching experiment can occur under irradiation (long irradiation time).

In addition, it can be chosen to focus either on the electronic impact by irradiating with gamma sources or light particles (He^{2+}), either on the ballistic effects by using heavy particles irradiation at low energies:

- Irradiations of inactive R7T7 by gold ions have been performed to simulate the ballistic damage induced by the recoil nuclei of alpha decays. These irradiation conditions were shown to simulate correctly the variation of macroscopic properties induced by alpha decays. Short leaching tests were performed to evaluate the effect of radiation on the initial alteration rate [Peuget et al. (2007)].
- Gamma irradiation of inactive glasses by ^{60}Co sources have been used to focus on electronic effects occurring during gamma transitions, beta and alpha decays, as the main interaction mode is dominated by Compton diffusion. This kind of irradiation system reproduces very well gamma transitions and beta decays, but is less representative of the alpha emission due to its lower linear energy transfer value [Rolland et al., (2013)] [Rolland et al., (2013)bis].

3. Examples to illustrate the methodology

3.1. Irradiation effect assessment on the initial rate of alteration r_0

The initial glass alteration rates have been determined by Soxhlet-mode dynamic leach testing at 100 °C, for 28 days, by monitoring the release of glass alteration tracer elements (B, Na, Li, Mo) and by weight loss. This study focuses on the alpha radiation effects as it is the main contributor on the R7T7 glass after a three hundred year period [Peuget et al. (2007)].

Concerning the influence of alpha activity, the results, obtained and presented in figure 2-a, show r_0 values centred in the range of initial dissolution rates of inactive samples. For the alpha activity of a fresh glass (about 10^9 $Bq.g^{-1}$), the values measured on $^{238/239}Pu$, ^{241}Am and ^{244}Cm-doped glasses are also consistent with the inactive values. The data thus suggest that the alpha activity in the range covered by the studied glasses, i.e. the whole range of alpha activity of a glass package under disposal conditions, does not significantly affect the initial dissolution rate of the glass.

Concerning the effect of alpha decay dose, initial dissolution rate r_0 has been measured on the different ^{244}Cm-doped glasses. In order to cover the entire range of alpha decay doses sustained by an industrial glass under disposal conditions, external irradiations with heavy ions have been performed on inactive samples. The results (figure 2-b) show that the alpha decay dose does not modify the initial dissolution rate significantly, considering a measurement uncertainty of 20%.

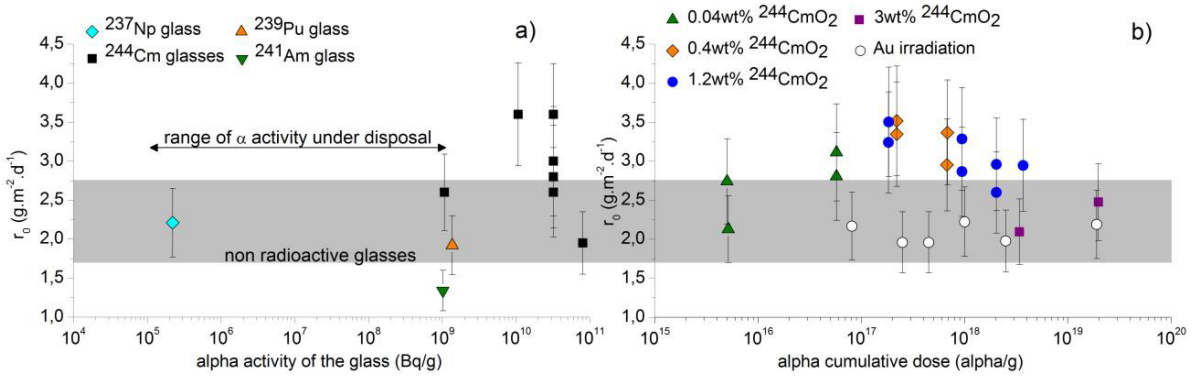

Fig. 2. Initial leaching rate r_0 versus: (a) alpha activity of the glass, and (b) alpha cumulative dose. Comparison with the r_0 obtained of non-radioactive glasses (grey area).

Finally neither the electronic nor the nuclear interactions induced by these irradiations affect significantly the initial glass leaching rate, in terms of both dose rate and cumulative dose. First, this conclusion means that reactive species formed by radiolysis (which could modify complexation reaction equilibria in solution, redox potential or

surface sorption ability) do not modify the hydrolysis reaction energy [Advocat et al. (2001)]. Second, this absence of irradiation effect also indicates that the glass structure is not changed enough by electronic and nuclear interactions to affect its chemical reactivity during the first instants. However, modifications on macroscopic (density, mechanical properties) and structural glass properties (boron coordination number variation, decrease in the Si-O-Si angle value, slight depolymerisation of the silicate network) have been observed under cumulative alpha decays [Peuget et al. (2014)]. Nevertheless, the initial rate, which is mainly dependant of the Si-O binding hydrolysis, does not depend on of the local geometry of the network polyhedra, as described by modelling studies [Jégou (1998)]. Thus, the slight angle variations of silicate tetrahedra and the slight network depolymerisation observed after irradiation are not important enough to induce any significant changes in the initial chemical reactivity between glass and water.

3.2. Residual alteration rate r_r of a relevant alpha doped glass

The residual alteration rate regime of a ^{239}Pu-doped glass has been studied by a static leaching experiment at 90°C, for 1200 days and at a high surface-area-to-volume ratio (S/V = 20 cm^{-1}). The alteration rate is monitored from solution analyses by the release of glass alteration tracer elements (B, Na and Li). Radiation effects on the leached glass and its gel network are characterized by SEM and TEM analyses. Plutonium releases are also measured by radiometry and its chemical oxidation state is assessed by measuring the pH and reduction-oxidation potential of the leachate [Rolland et al. (2013)].

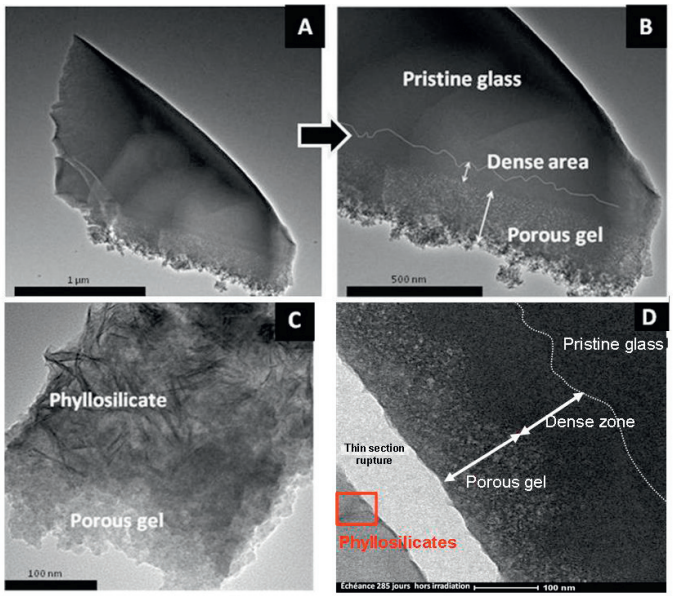

Fig. 3. Bright-field TEM images of the ^{239}Pu-doped glass altered layer (a)(b)(c) and of a nonradioactive R7T7 glass altered layer (d) reference (HV=200 kV).

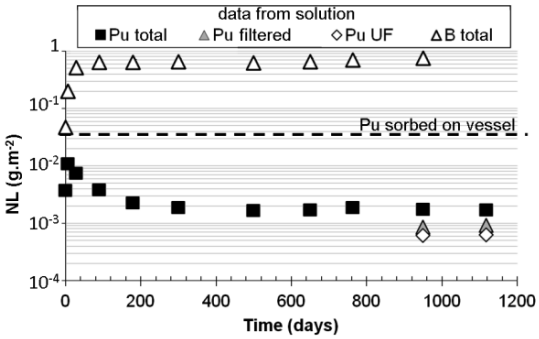

Fig. 4. Total, filtered and ultrafiltered (UF) plutonium concentrations measured in solution versus time (expressed in $g.m^{-2}$). Comparison with boron releases. The dotted line represents the amount of Pu sorbed on the vessel and determined from rinses, expressed in NL.

Data obtained from solution and solid analyses show that the residual rate is not significantly affected by the alpha dose rate (150 $Gy.h^{-1}$) and the local irradiation field in water (i.e high linear energy transfer). Moreover, the morphology and protective properties of the altered layer formed under these conditions are similar to those of the inactive SON68 glass, as presented in figure 3. These results are consistent with similar studies performed on nonradioactive SON68 glass under external gamma irradiation at 50 $Gy.h^{-1}$, where no direct effects of such irradiation were observed on the glass residual alteration rates [Rolland et al. (2013)bis].

Concerning the plutonium behavior, the presence of plutonium colloids is evidenced in the leachate and the soluble Pu concentration suggest that Pu releases are not controlled by the solubility of a stable well defined Pu(IV) hydroxide phase, but by a phase presenting a lower solubility limit. However, as presented in figure 4, plutonium remains strongly retained/sorbed in the altered layer (with a retention factor of 95%).

4. Conclusions and prospects

The effect of radioactivity on the glass leaching behavior is studied by considering both doped materials and non radioactive glasses externally irradiated. The influence of the radiation nature (i.e. α, β, γ) and the effects of the integrated dose and of the dose rate on glass leaching behavior have been investigated by studying radionuclides doped glasses and externally irradiated inactive glasses.

The first results presented here and focusing on the initial alteration rate did not show significant effects of alpha dose rate and alpha cumulative dose. Concerning the cumulative dose, this could be understood by considering that the hydrolysis reaction is not sensitive to the slight structural changes observed on the solid structure after alpha decay irradiation.

The second results presented concern the behavior of a ^{239}Pu-doped glass having an alpha dose rate corresponding to a typical HLW glass after about 1500 years. In this case, no effect on the kinetics has been observed, nor on the altered layer morphology. Moreover, the plutonium appears to be highly retained/sorbed in the alteration layer (95%).

In prospect, further studies would be necessary to assess the relative impact of redox conditions, groundwater and environmental materials surrounding a geological repository both on the radioactive glass leaching behavior and on redox-sensitive radioelements (Pu, Tc, Np).

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